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Solvent effect on the volume of activation and volume of the Diels-Alder reaction

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Abstract

Volumes of activation, ΔV≠, and reaction, ΔV, partial molar volumes, V̄, and enthalpies of solution, ΔsolH, were determined for tetracyanoethylene, cyclopentadiene, 1,3-butadiene, trans, trans-1,4-diphenyl-1,3-butadiene and their Diels-Alder adducts at 25°C in some solvents of π- and n-donor type. The values of the activation and reaction volumes were exceptionally small in the former type of solvents. Large solvent effects on ΔsolHTCNE (up to 26 kJ mol-1), V̄TCNE, ΔV and δV≠ (up to 11 cm3mol-1) were observed in aromatic solvents and these values are linearly correlated with each other. Poor correlations were found for n-donor solvents, but a linear dependence between ΔV and δr-nH (enthalpy of reaction) was obtained for all solvents. © 2001 John Wiley & Sons, Ltd.

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Keywords

Solvent effect, Tetracyanoethylene, Volume of activation, Volume of reaction